

I need not here enlarge upon the additional value which these structural and physiological considerations afford, to the character of “perforation” or “non-perforation” in the shells of Brachiopoda. The importance of this character in systematic arrangement will plainly appear, I think, from the details which I have published in the Introduction to Mr. Davidson's Monograph already referred to.

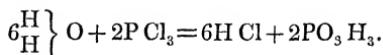
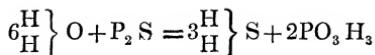
II. “On a new Series of Sulphuretted Acids.” By Dr. AUGUST KEKULÉ. Communicated by Dr. SHARPEY, Sec. R.S.
Received April 5, 1854.

Adopting the idea that the series of organic compounds of which sulphuretted hydrogen is the type, corresponds in every respect with the series of which water is the type, I concluded that not only mercaptans and neutral sulphides which correspond to the alcohols and ethers, but also compounds corresponding to the acids, anhydrous acids and ethers of acids might be produced; I therefore endeavoured to obtain reactions which would enable me to replace oxygen in the compounds of the latter series by sulphur.

Such reactions are produced by the compounds of sulphur with phosphorus—the tersulphide ($P_2 S_3$) and the pentasulphide ($P_2 S_5$)—which are easily obtained by fusing together amorphous phosphorus and sulphur in an atmosphere of carbonic acid; no explosion takes place, although the combination is attended with a very violent action.

Experiment has proved that these combinations of sulphur and phosphorus act on the members of the series of water in the same manner (although less violently) as the corresponding compounds of chlorine and phosphorus;—however, with this difference, that by using the chlorine compounds the product is resolved into *two* groups of atoms, while by using the sulphur compounds there is obtained only *one* group; a peculiarity, which, according to the bibasic nature of sulphur, must have been expected. By acting on these compounds of sulphur and phosphorus with water one atom of sulphu-

retted hydrogen is obtained, while the chlorides give two atoms of hydrochloric acid,



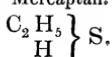
Similar reactions are observed with organic compounds belonging to the series of water with the formation of phosphorous and phosphoric acids respectively, or a copulated acid. By acting in this way, the following series of sulphuretted organic compounds is obtained, by the side of which are placed for comparison the products formed by the action of the chlorides of phosphorus on the same substances.

Sulphuretted Hydrogen.



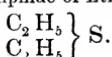
Hydrochloric Acid.
2H Cl.

Mercaptan.



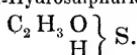
Chloride of Ethyl+Hydrochloric Acid.
 $\text{C}_2 \text{H}_5 \text{Cl} + \text{H Cl.}$

Sulphide of Ethyl.



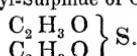
Chloride of Ethyl.
 $2\text{C}_2 \text{H}_5 \text{Cl.}$

Othyl-Hydrosulphuric Acid.



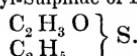
Chloride of Othyl+Hydrochloric Acid.
 $\text{C}_2 \text{H}_3 \text{O, Cl} + \text{H Cl.}$

Othyl-Sulphide of Othyl.



Chloride of Othyl.
 $2\text{C}_2 \text{H}_3 \text{O, Cl.}$

Othyl-Sulphide of Ethyl.



Chloride of Othyl+Chloride of Ethyl.
 $\text{C}_2 \text{H}_3 \text{O, Cl} + \text{C}_2 \text{H}_5 \text{Cl.}$

Mercaptan is obtained by the action of tersulphide or pentasulphide of phosphorus on alcohol with extreme facility. Sulphide of ethyl may also be prepared by acting on ether in a similar manner.

Thiacetic Acid.—*Sulphuretted Acetic Acid*.—has been obtained by me by acting on monohydrated acetic acid with tersulphide of phosphorus. It is a colourless liquid, boiling at about 93°C. , and has a peculiar odour resembling sulphuretted hydrogen and acetic

acid. It dissolves potassium in the cold and zinc on heating with the evolution of hydrogen, and gives with lead a salt less soluble than the ordinary acetate, so that it gives a precipitate with acetate of lead. By recrystallization from water or alcohol, the lead salt is obtained in fine silky needles, which, though quite colourless at first, are rapidly decomposed (whether in solution or in the solid form) with the formation of sulphide of lead.

By analysis I found the lead salt contained—

Lead 58.8 per cent. Theory requires 58.0 per cent.

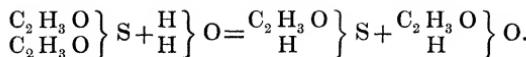
The acid contained—

Sulphur 41.3 per cent. Theory requires 42.1 per cent.

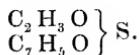
Thiacetic acid is also formed in small quantity and by secondary action, by distilling pentasulphide of phosphorus with fused acetate of soda. Pentachloride of phosphorus gives a violent reaction with thiatic acid, yielding sulphochloride of phosphorus, chloride of oethyl, and hydrochloric acid,



Thiacetate of Oethyl.—*Sulphide of Oethyl.*—*Anhydrous Sulphuretted Acetic Acid.*—Pentasulphide of phosphorus acts but very feebly upon anhydrous acetic acid in the cold, but on heating a violent reaction takes place. By distilling the product, the anhydrous acid is obtained in the form of a colourless liquid, boiling at about 121° C., and having an odour greatly resembling sulphuretted acetic acid. On mixing with water it falls to the bottom, without, at first, suffering any change; on standing, however, it is slowly dissolved and decomposed into sulphuretted acetic acid and ordinary acetic acid. This change takes place much more rapidly on heating,



It appears that anhydrous sulphuretted acetic acid is also produced by acting on the oethyl-sulphide of lead with chloride of oethyl, at all events chloride of lead is formed. Chloride of benzoyle gives with the lead salt a similar reaction, and it is probable that an intermediate sulphuretted acid is formed, having the formula



Thiacetate of Ethyl.—Sulphuretted Acetic Ether.—This compound may be prepared by the action of pentasulphide of phosphorus on acetic ether. It is a liquid lighter than water, and possesses an odour resembling acetic ether and sulphuretted hydrogen. It boils at about 80° C.

It will be seen that the action of tersulphide and pentasulphide of phosphorus above described produces sulphuretted organic compounds by substituting sulphur for oxygen. The compounds obtained in this way may also be formed by replacing one or two atoms of hydrogen in sulphuretted hydrogen (H_2S), or one or two atoms of metal in sulphide of potassium (K_2S), or in sulphide of hydrogen and potassium (KHS), by organic radicals. Mercaptan and the sulphides of alcohol radicals have, in fact, been long obtained in this manner.

The formation of a sulphuretted compound containing an acid radical has been observed by Gerhardt by acting on sulphide of lead with chloride of oethyl. I have not made many experiments of this kind, but I have observed that chloride of benzoyle is not decomposed by sulphuretted hydrogen, while it (as well as chloride of oethyl) gives a reaction with sulphide of hydrogen and potassium yielding chloride of potassium.

I am continuing these researches, and believe the above reactions will furnish many new compounds, and will tend to complete our knowledge of some of those organic and inorganic compounds now known.

The Society then adjourned to the 27th of April.